

Amorphous metal-organic frameworks loaded on BiVO₄ photoanodes with unique internal metal-like structure for promoting photoelectrochemical water splitting

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ABSTRACT

Although ferrocene (Fc) based Metal-Organic Frameworks (MOFs) can act as oxygen evolution co-catalysts (OECs) for improvement of catalytic reactivity, the poor conductivity and lack of highly active metal sites limit its further application in photoelectrochemical (PEC) water splitting. Herein, the amorphous NiFc-MOF was grafted on BiVO₄ photoanode (BiVO₄@aNiFc-MOFs) for efficient PEC water splitting. This novel BiVO₄@aNiFc-MOFs exhibits high current density of 4.34 mA cm⁻² at 1.23 V_{RHE} and relative low onset potential of 0.223 V_{RHE}. The subsequent characterizations demonstrate that Ni species with metal-like state in bulk of aNiFc-MOFs form strong metal-support interaction with BiVO₄, thereby promoting the interfacial charge transfer. Moreover, the surface of aNiFc-MOFs is short-range ordered with abundant coordinatively unsaturated Ni sites, creating a more favorable pathway for oxygen evolution reaction from thermodynamics. This work provides a simple method to design photoanodes with efficient OECs of amorphous MOFs for feasible PEC water splitting application.

1. Introduction

Photoelectrochemical (PEC) hydrogen generation using solar energy is considered as the most promising strategy to solve the energy crisis [1, 2]. However, the four electron process of water oxidation is thermodynamical unfavorable, resulting in the oxygen evolution reaction (OER) being the rate-determining step [3]. Therefore, much attention was paid to developing efficient metal oxide/sulfide photoanode materials such as ZnO [4,5], TiO₂ [6,7], α-Fe₂O₃ [8,9], WO₃ [10], BiVO₄ [11,12] and CdS [13,14]. Among them, BiVO₄-based photoanode with higher theoretical solar-to-hydrogen conversion efficiency (9.2%) and photocurrent (7.5 mA cm⁻² under standard AM 1.5 solar light irradiation) attracted significant interest in PEC water splitting reaction [15]. Unfortunately, due to the relatively low carrier mobility of 0.044 cm²·V⁻¹·s⁻¹ and a short hole diffusion distance of 70 nm [16,17], severe photogenerated charges recombination occurred both in the bulk and on the surface of BiVO₄. Additionally, the rate constant of OER of BiVO₄ calculated from transient absorption spectroscopy is approximately 1.4 s⁻¹ [18], indicating a sluggish water oxidation kinetics of pristine BiVO₄ photoanode.

These inherent defects lead to serious lower photocurrent density and efficiency than the theoretical values, thereby limiting its practical application.

To enhance the PEC water splitting activity of BiVO₄ photoanodes, construction of heterogeneous interface, crystalline engineering, hybrid atoms doping and OECs modification have been extensively investigated [19–26]. Among them, OECs can not only provide additional active sites to decrease the activation energy of OER but also passivate the surface states for suppressing charge recombination, which is considered as the most efficient strategy to improve the PEC water splitting activity. Although precious metal catalysts such as IrO₂ and RuO₂ shown satisfactory OER catalytic activity, high cost limited their widespread application [27]. Recently, MOFs constructed from transition metal ions/clusters coordinated with organic ligands could act as highly efficient OECs owing to ordered structures, uniform dispersion of active sites, periodic arrangement of atoms, and high tenability [28–31]. The transition-metal complex ferrocene (Fc) and its derivatives are sandwich like aromatic organometallic compounds, which are formed by combining two cyclopentadienes and one Fe²⁺ via strong ‘cation-π’ and

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' π - π ' interactions. Attributing to remarkable molecular structural stability and redox activity, Fc-based MOFs are widely applied in the field of catalysis [32,33]. Nevertheless, on one hand, the primary building blocks of the structure comprise O- donor redox-inactive organic ligands, which inefficiently facilitate routes for charge transfer [34,35]. On the other hand, the Fe atoms in Fc serve as bridging units with unsatisfied catalytic activity, which limited the availability of metal sites capable of functioning as active centers in MOFs [36]. Thus, these Fc-based MOFs OEC still faced problems involving poor conductivity of MOF skeletons and lack of highly active metal sites.

Various methods including post-modifying metal/organic components [37] and introducing additional active sites into MOFs [38] have been developed to address these challenges. Current study demonstrated that amorphization of long-range ordered crystalline MOFs (c-MOFs) could lead to more active unsaturated sites, higher conductivity, and improved photoluminescence efficiency [39–41]. During the amorphization process, the charge density between defective sites and adjacent coordination atoms undergoes redistribution, optimizing the local electronic structure to promote charge transfer and redox kinetics of catalysis [42]. Thus, it inspires us to synthesize the amorphous Fc-based MOFs on the BiVO_4 photoanode as highly efficient OECs.

In this work, we have modulated the crystallinity of Fc-based MOFs coordinated with Ni (NiFc-MOFs) via simply varying the concentration of compositional units in precursors. The amorphous NiFc-MOFs (aNiFc-MOFs) loaded on the BiVO_4 photoanode (BiVO_4 @aNiFc-MOFs) exhibit the highest PEC water splitting activity. Structure characterizations indicated that the surface of aNiFc-MOFs are short-range ordered with abundant coordinatively unsaturated Ni sites. While, its internal atomic structure of Ni displays a metal-like state, which forms a strong metal-support interaction (SMSI) with the supporter semiconductor BiVO_4 . The following carrier kinetic characterizations and density functional theory (DFT) calculations demonstrated that such unique structure of BiVO_4 @aNiFc-MOFs with SMSI greatly facilitated the interfacial charge transfer and separation. Meanwhile, the BiVO_4 @aNiFc-MOFs with abundant coordinatively unsaturated Ni sites could provide additional open metal sites for OER, resulting in a more favorable pathway for adsorbing O adsorbates, especially for the rate-determining step of adsorbing $\cdot\text{OOH}$. Consequently, BiVO_4 @aNiFc-MOFs photoanode achieves an excellent photocurrent density of 4.34 mA cm^{-2} at 1.23 V versus the RHE, which is 3.3 times higher than that of pristine BiVO_4 electrode (1.31 mA cm^{-2}), while its onset potential (0.223 V) is 269 mV lower than that of BiVO_4 (0.492 V). Thus, this work provides a simple method to prepare efficient, stable, and cost-effective BiVO_4 based photoanodes with amorphous MOFs (a-MOFs) OECs.

2. Experimental section

2.1. Chemicals and materials

1,1'-ferrocene dicarboxylic acid [FcDA, 98.0%], acetone ($\text{C}_3\text{H}_6\text{O}$, AR) and vanadyl acetylacetonate [$\text{VO}(\text{acac})_2$, 99.0%] were purchased from Shanghai Macklin Biochemical Co., Ltd. Potassium iodide (KI, 99.0%), p-benzoquinone (99.5%, HPLC), bismuthnitrate pentahydrate [$\text{Bi}(\text{NO}_3)_3 \cdot 5 \text{ H}_2\text{O}$, 99.0%], dimethyl sulfoxide (DMSO, 99.8%), boric acid (H_3BO_3 , 99.5%), sodium sulfite (Na_2SO_3 , 98.0%), sodium hydroxide (NaOH, AR) were supplied by Shanghai Aladdin Biochemical Technology Co., Ltd. Ethanol (HPLC), N, N-dimethylformamide (DMF, $\geq 99.5\%$) were obtained from Sinopharm Chemical Reagent Co., Ltd. Concentrated nitric acid (HNO_3 , 68.0 wt%), potassium hydroxide (KOH, AR), nickel (II) chloride hexahydrate ($\text{NiCl}_2 \cdot 6 \text{ H}_2\text{O}$, AR) were supplied by Nanjing Chemical Reagent Co., Ltd. All chemicals need not be further purified during the whole experiment.

2.2. Preparation of BiVO_4 @aNiFc-MOFs photoanodes

2.2.1. Synthesis of BiVO_4 photoanodes

Before synthesizing, fluorine doped SnO_2 (FTO) conductive glass was ultrasonized in acetone, ethanol and deionized water for 30 min, respectively. The BiVO_4 photoanodes were fabricated by the electrochemical deposition method in a typical three-electrode cell [43]. Briefly, the BiOI electrodes were firstly prepared at the constant potential (-0.1 V vs. Ag/AgCl for 150 s) using $\text{Bi}(\text{NO}_3)_3 \cdot 5 \text{ H}_2\text{O}$ (40.0 mM) and KI (0.4 M) solution (pH 1.7). After thoroughly rinsing with deionized water and drying at room temperature, 100 μL vanadium precursor solution [DMSO solution containing 0.2 M $\text{VO}(\text{acac})_2$] was dripped onto the BiOI electrodes. Then, the nanofilms were heated in muffle furnace for 2 h (450°C , ramping rate 2°C/min). The obtained electrodes were immersed in NaOH solution (1.0 M) for 30 min to remove the V_2O_5 on the surface of BiVO_4 .

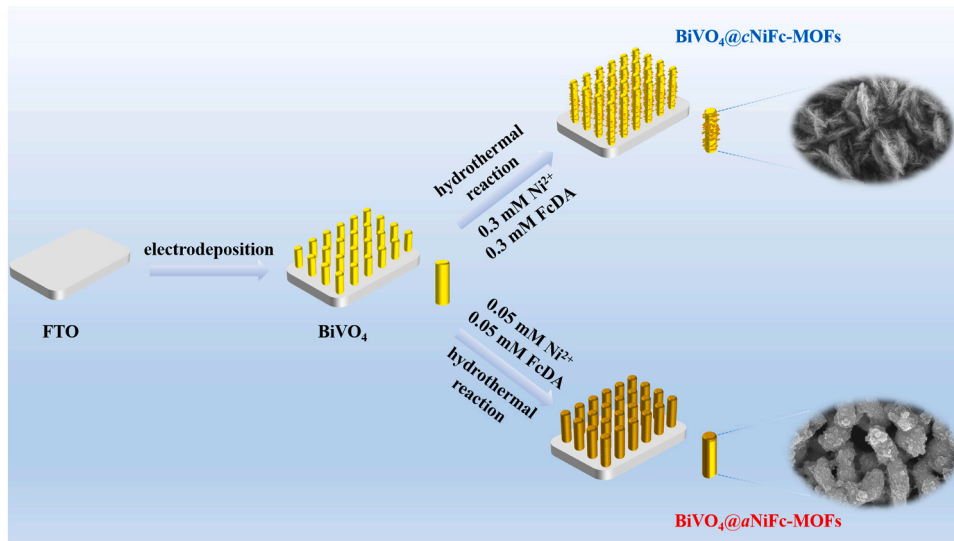
2.2.2. Synthesis of BiVO_4 @aNiFc-MOFs photoanodes

In this work, BiVO_4 @aNiFc-MOFs photoanodes were synthesized by a hydrothermal method. 0.05 mM FcDA was dissolved in 8 mL DMF, and then 4 mL 0.05 mM $\text{NiCl}_2 \cdot 6 \text{ H}_2\text{O}$ aqueous solution was added in the mixture. After stirring for 10 min, the mixed solution was transferred into a 25 mL Teflon reactor with a piece of pre-fabricated BiVO_4 photoanode vertically submerged in it and heated at 125°C for 12 h. The obtained sample (BiVO_4 @aNiFc-MOFs) was rinsed with deionized water and dried in vacuum oven at 60°C for at least 12 h.

As comparisons, the crystalline NiFc-MOFs (cNiFc-MOFs) loaded on the BiVO_4 photoanode (BiVO_4 @cNiFc-MOFs) was also prepared. The preparation method of BiVO_4 @cNiFc-MOFs photoanodes was similar to that of BiVO_4 @aNiFc-MOFs mentioned above, except for that the concentration of FcDA and $\text{NiCl}_2 \cdot 6 \text{ H}_2\text{O}$ solution was 0.3 mM.

2.3. Characterizations

The morphology and micro-structure of samples were observed by Scanning electron microscopy (SEM, Zeiss Sigma 300) and Transmission electron microscopy (TEM, FEI Talos F200X). Energy-dispersive X-ray spectra (EDS) was determined to analyze the elements distribution on photoanode surface by using Super-X (China). The content of each element of the catalysts loaded on FTO was quantified by Inductively coupled plasma mass spectrometry (ICP-MS). The crystallinity and crystal face of samples were identified by the X-ray diffractometer (XRD, Cu- α radiation, X'TRA, Switzerland) in the range of 10 – 70° (2θ) at a scanning rate of 5 min^{-1} . Moreover, surface chemical composition and the valence states of elements were analyzed by X-ray photoelectron spectroscopy (XPS, PHI 5000 VersaProbe III with AES, ULVAC-PHI, Japan) using Al- α X-ray source, and all binding energies were calibrated by a C 1 s peak as standard (284.8 eV). The XPS argon-ion sputtering tests were performed with a practical sputter time of 30 seconds per cycle, totaling six cycles. The functional groups of samples were characterized by Fourier transform infrared spectrometer (FTIR, Thermo Scientific Nicolet iS20, America). The UV–vis diffuse reflectance spectra (UV–vis) was collected by the UV–vis spectrophotometer equipped with an integration sphere (UV-2600, Shimadzu, Japan) to evaluate the optical properties of photoanodes. The kinetics of electron separation and transfer were assessed by the steady-state Photoluminescence spectroscopy (PL) and Time-resolved photoluminescence spectroscopy (TRPL) with an excitation laser at 405 nm. Electron paramagnetic resonance (EPR) spectra of the photoanodes were recorded on Bruker EMX micro. The Ni K-edge X-ray absorption spectroscopy (XAS) experiments were performed and analyzed with the Athena and Artemis programs of the Demeter data analysis packages that utilizes the FEFF6 program to fit the EXAFS data.



Scheme 1. Schematic illustration of preparation process of $\text{BiVO}_4\text{@cNiFc-MOFs}$ and $\text{BiVO}_4\text{@aNiFc-MOFs}$.

2.4. Photoelectrochemical measurements

The PEC measurements of photoanodes were carried out by an electrochemical workstation (CHI760E, China) with a typical three-electrode configuration under illumination conditions (AM 1.5 G, 100 mW cm^{-2}). An aqueous solution of 0.5 M potassium borate solution (KBI) electrolyte (pH 9.3) was used as the electrolyte.

Linear sweep voltammetry (LSV) was conducted at the scanning rate of 10 mV/s and the electrolyte was aerated with N_2 for at least 30 min before the test. The incident photon-to-current conversion efficiency (IPCE) is determined by using the light source with a motorized monochromator. The stability test was carried out under 1.23 V vs. RHE. The hydrogen and oxygen were collected by Labsolar-6A system (Beijing Perfectlight), and the gas production was determined by gas chromatography (GC9790II, Fuli Instruments) every 20 min. The light-dark J-t test was conducted under 1.23 V vs. RHE and the shutter controller was set to switch every 30 s. Photoelectrochemical Impedance Spectroscopy (PEIS) was measured with a frequency range from 10^{-1} to 10^6 Hz at $0.2 \text{ V}_{\text{RHE}}$ (AM 1.5 G illumination). Mott-Schottky (M-S) plots were collected in the dark at a frequency of 1 kHz . Cyclic voltammetry (CV) measurements were carried out at scanning rate from 10 to 50 mV/s (potential range from 0.8 to $1.0 \text{ V}_{\text{RHE}}$). The electrochemical double layer capacitances (C_{dl}) could be calculated by linear fitting of the current D-values under different scanning rates (half of the slope). Both charge separation efficiencies (η_{sep}) and charge injection efficiencies (η_{inj}) were identified by adding $0.2 \text{ M Na}_2\text{SO}_3$ (holes scavenger) into KBI electrolyte.

The potential conversion formula of RHE and Ag/AgCl is as follows [44]:

$$E_{\text{RHE}} = E_{\text{Ag/AgCl}} + 0.0591 \times \text{pH} + E^0 \quad (1)$$

Where E^0 is the standard electrode potential of Ag/AgCl reference electrode at 25°C (0.1976 V), E_{RHE} refers to the converted potential vs. RHE and $E_{\text{Ag/AgCl}}$ is the potential applied in a three-electrode system with Ag/AgCl as a reference electrode.

Incident photon to current conversion efficiency (IPCE) [45]:

$$\text{IPCE}(\%) = \frac{J_{\text{ph}} \times 1240}{P_{\text{mono}} \times \lambda} \quad (2)$$

Where J_{ph} is the measured photocurrent density ($\text{mA}\cdot\text{cm}^{-2}$), P_{mono} is the power density of monochromatic light ($\text{mW}\cdot\text{cm}^{-2}$), λ is the incident light wavelength (nm).

Applied bias photon to current efficiency (ABPE) [46]:

$$\text{ABPE} = J \times \frac{1.23 - V_b}{P_{\text{light}}} \quad (3)$$

where J is the LSV photocurrent density ($\text{mA}\cdot\text{cm}^{-2}$), V_b is the applied voltage (V vs. RHE), and P_{light} is the intensity of incident light ($100 \text{ mW}\cdot\text{cm}^{-2}$, AM 1.5 G).

The Faradaic efficiency can be determined as [47]:

$$\eta_{\text{O}_2} = \frac{4Fn_{\text{O}_2}}{Q} \quad (4)$$

$$\eta_{\text{H}_2} = \frac{2Fn_{\text{H}_2}}{Q} \quad (5)$$

Where η_{O_2} and η_{H_2} is the Faraday efficiency, F is Faraday constant ($96485 \text{ C}\cdot\text{mol}^{-1}$), n_{O_2} and n_{H_2} is the production of hydrogen and oxygen (mol), Q is the amount of charges generated by photocarriers (C).

The carrier concentration (N_d) can be determined as [47]:

$$N_d = \frac{2}{e\epsilon_0\epsilon_r} \left(\frac{dC^{-2}}{dV} \right)^{-1} \quad (6)$$

Where N_d is carrier densities (cm^{-3}), e is the electron charge ($1.6 \times 10^{-19} \text{ C}$), ϵ_0 is vacuum dielectric constant ($8.85 \times 10^{-14} \text{ F}\cdot\text{cm}^{-1}$), ϵ_r is the relative dielectric constant of BiVO_4 (68), $\frac{dC^{-2}}{dV}$ is the slope of M-S plots ($\text{F}^{-2}\cdot\text{cm}^4\cdot\text{V}^{-1}$).

The separation efficiencies of photo-generated electron (η_{sep}) and hole pairs and surface charge injection efficiencies (η_{inj}) can be determined as [46]:

$$\eta_{\text{sep}} = \frac{J_{\text{Na}_2\text{SO}_3}}{J_{\text{abs}}} \quad (7)$$

$$\eta_{\text{inj}} = \frac{J_{\text{H}_2\text{O}}}{J_{\text{Na}_2\text{SO}_3}} \quad (8)$$

Where J_{abs} is the photocurrent density ($\text{mA}\cdot\text{cm}^{-2}$) when the percentage of absorbed photons to current is 100%, $J_{\text{Na}_2\text{SO}_3}$ and $J_{\text{H}_2\text{O}}$ are the photocurrent density ($\text{mA}\cdot\text{cm}^{-2}$) for sulfite oxidation and water oxidation, respectively.

2.5. DFT calculations

A simplified model of aNiFc-MOFs on the BiVO_4 was constructed,

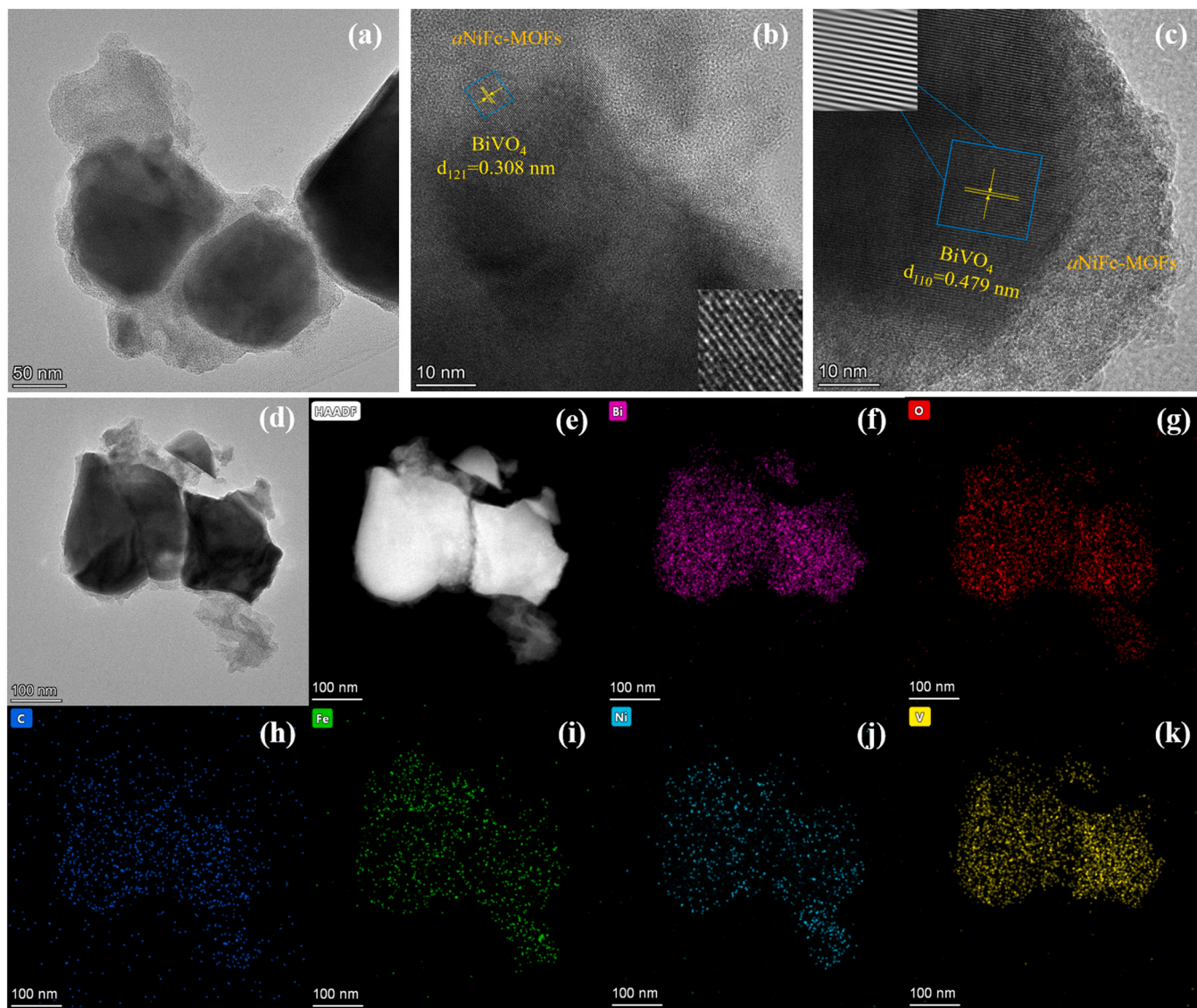


Fig. 1. (a)–(d) TEM images of BiVO₄@aNiFc-MOFs photoanode. (e) HAADF of BiVO₄@aNiFc-MOFs photoanode. EDS elemental mapping images of photoanode (f) Bi, (g) O, (h) C, (i) Fe, (j) Ni, (k) V.

which could directly gain insights into the role of aNiFc-MOFs with abundant coordinatively unsaturated Ni sites in mediating each step of OER process. The free energy associated with each step of the OER was calculated using density functional theory (DFT) within the Vienna Ab Initio Package (VASP). The PBE function within the generalized gradient approximation (GGA) method was employed to account for exchange-correlation effects. The projected augmented wave (PAW) method, with a plane wave expansion set and an energy cutoff of 500 eV, was utilized to incorporate core-valence interactions. Brillouin zone sampling was conducted with a $3 \times 3 \times 1$ Monkhorst-Pack grid of k-points. To prevent periodic interactions, a vacuum layer extending 15 Å above the surface was introduced. The structural optimization iterated until electronic energy and force changes were both smaller than 1.0×10^{-4} eV and 0.02 eV Å⁻¹, respectively.

The Gibbs free energy change (ΔG) of each OER step was calculated using the following formula:

$$\Delta G = \Delta E + \Delta ZPE - T\Delta S \quad (9)$$

where ΔE is the obtained electronic energy difference, ΔZPE is the zero-point energy difference, T is the temperature (298.15 K) and ΔS is the entropy change. After frequency calculation, ZPE can be obtained

according to:

$$ZPE = \frac{1}{2} \sum h\nu_i \quad (10)$$

The TS values of adsorbed species can be calculated based on the vibrational frequencies by:

$$TS = k_B T \left[\sum_k \ln \left(\frac{1}{1 - e^{-\frac{h\nu_k}{k_B T}}} \right) + \sum_k \frac{h\nu_k}{k_B T} \cdot \frac{1}{(e^{\frac{h\nu_k}{k_B T}} - 1)} + 1 \right] \quad (11)$$

3. Results and discussion

3.1. Morphology and structure characterization of BiVO₄@aNiFc-MOFs photoanode

The BiVO₄@aNiFc-MOFs photoanodes were fabricated via a versatile method combining the electrodeposition and hydrothermal reaction (Scheme 1). The crystalline degree of NiFc-MOFs was modulated by simply controlling the concentration of compositional metal ion (NiCl₂·6 H₂O) and organic linker (FcDA) precursors. Based on the analysis of crystalline-performance relationship (Text S1), amorphous NiFc-MOFs and crystalline NiFc-MOFs on BiVO₄ photoanodes

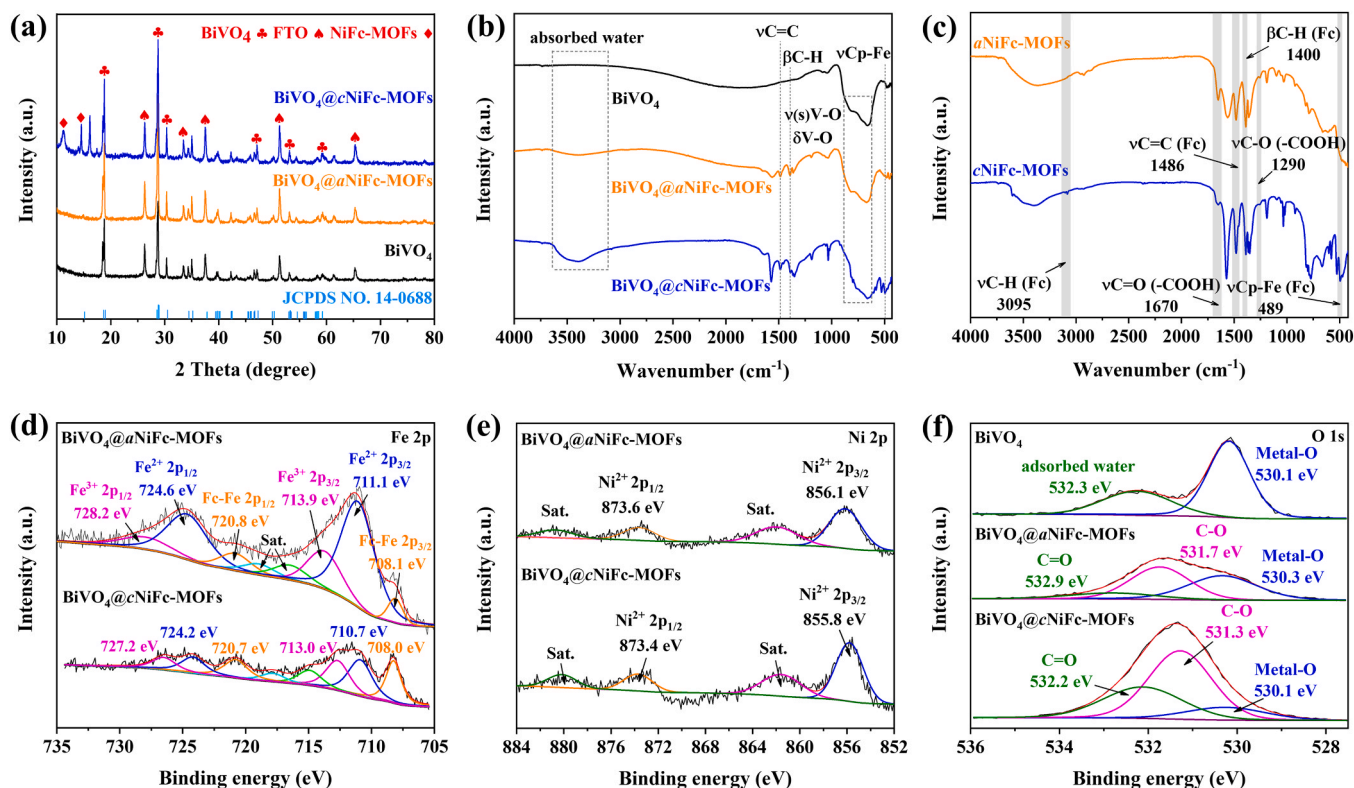


Fig. 2. (a) XRD patterns. FTIR spectra of (b) BiVO₄, BiVO₄@aNiFc-MOFs and BiVO₄@cNiFc-MOFs photoanodes. (c) amorphous and crystalline NiFc-MOF powders. High-resolution XPS spectra of (d) Fe 2p, (e) Ni 2p and (f) O 1 s.

(BiVO₄@aNiFc-MOFs and BiVO₄@cNiFc-MOFs) prepared with precursor (0.05 mM and 0.3 mM, respectively) are selected for further studies.

SEM image shows that loading of aNiFc-MOFs significantly increased the surface roughness of nanorods-like structured BiVO₄ (Fig. S2a, b), while the cNiFc-MOFs vertically grown on the BiVO₄ are dense and uniform nanosheets (Fig. S2c). Such morphology difference indicates that the aNiFc-MOFs are amorphously coated on the surface of BiVO₄. TEM images of BiVO₄@aNiFc-MOFs photoanode further confirm the amorphous structure of the NiFc-MOFs intimately coated on the surface of BiVO₄. The lattice fringes of 0.308 nm in Fig. 1b and 0.483 nm in Fig. 1c are corresponded to (121) and (110) plane of monoclinic BiVO₄ [11], respectively. However, only a well coated aNiFc-MOFs layer on BiVO₄ is evidently observed in all TEM images, with no obvious lattice fringes being visible (Fig. 1a-d). Moreover, the TEM-EDS (Fig. 1e-k) and SEM-EDS mappings (3) also indicate the uniform distribution of the aNiFc-MOFs on the surface of BiVO₄. The element contents of BiVO₄@aNiFc-MOFs photoanode are collected based on the TEM-EDS, SEM-EDS mappings and ICP-MS test (Fig. S3 and Table S1-2). The content of Ni in BiVO₄@aNiFc-MOFs is less than that of Fe (Ni:Fe ≈ 3:4), which is different from the typical atomic ratio of metal ion to Fe in Fc-based MOFs (1:1) [32,37], thereby indirectly proving the existence of Ni defects. In addition, compared with BiVO₄ photoanode, the XRD peaks of the BiVO₄@aNiFc-MOFs are not changed obviously (Fig. 2a). Both of them agreed well with the standard card of monoclinic BiVO₄ (JCPDS No.14-0688) [48]. However, two characteristic peaks of (400) and (001) plane of NiFc-MOFs were observed after loading of cNiFc-MOFs on BiVO₄. These results further confirmed the amorphous structure of the NiFc-MOFs on the surface of BiVO₄@aNiFc-MOFs photoanode.

The chemical composition and chemical state of samples are analyzed by using XPS and FTIR. The XPS survey spectra of BiVO₄@aNiFc-MOFs and BiVO₄@cNiFc-MOFs exhibit distinct characteristic peaks for the four elements (C, O, Fe, and Ni) (Fig. S4a). Meanwhile, the coated NiFc-MOFs mask the XPS signals from the underlying BiVO₄,

leading to the absence of peaks corresponding to the Bi and V (Fig. S4b, c). However, the strong absorption peaks at 700–910 cm⁻¹ ascribed to deformation bending and symmetrical stretching vibration of V-O of BiVO₄ [49,50] are shown in FTIR spectra for all samples (Fig. 2b). These experimental results indicate the successful synthesizing of BiVO₄ substrate and uniform wrapping of the surface aNiFc-MOFs/cNiFc-MOFs layer. The bands at 489 cm⁻¹, 1486 cm⁻¹ and 1400 cm⁻¹ (Fig. 2b) are respectively assigned to the stretching vibration of Cp-Fe (Cp = cyclopentadiene), C=C and the in-plane bending vibration of C-H in Fc ligand [32], suggesting the successful incorporation of Fc in BiVO₄@aNiFc-MOFs. XPS peaks of Fe 2p at 708.1 and 720.8 eV attributing to the divalent Fe (Fe²⁺ 2p_{3/2} and Fe²⁺ 2p_{1/2}) in Fc units (Fig. 2d) can also confirm the successful introduction of Fc. The detailed FTIR bands assignments of NiFc-MOFs are marked in Fig. 2c. Notably, compared with the aNiFc-MOFs, band of C=O (1670 cm⁻¹) stretching vibration of the ferrocenedicarboxylic groups nearly disappeared in the cNiFc-MOFs, indicating that plenty of carboxyl groups of the Fc units were not coordinated to metal Ni sites in aNiFc-MOFs [36]. Thus, these Ni sites might be coordinatively unsaturated. The Ni2p_{3/2} (856.1 eV) and Ni2p_{1/2} (873.6 eV) peaks with satellite signals of BiVO₄@aNiFc-MOFs can be ascribed to divalent state Ni coordinated with oxygen atoms in ferrocene units (Fig. 2e). Analysis of O 1 s spectra (Fig. 2f) indicates the existence of Metal-O (530.3 eV), C-O (531.7 eV) and C=O (532.9 eV), further suggesting the successful coordination between Ni²⁺ and carboxylic group of ferrocene units. Moreover, compared with those of BiVO₄@cNiFc-MOFs, the XPS characteristic peaks of Ni 2p and O1s in BiVO₄@aNiFc-MOFs shifted towards the higher binding energy, also revealing the changes of surface Ni coordination environment [51,52]. Specifically, the amorphization of NiFc-MOFs on BiVO₄@aNiFc-MOFs photoanode led to the formation of abundant coordinatively unsaturated Ni centers with a higher valent state [37].

For deeper comprehension of the unsaturated coordination environment of Ni atoms, the atomic and electronic structure of the BiVO₄@aNiFc-MOFs photoanode was investigated by EPR, the Ni K-

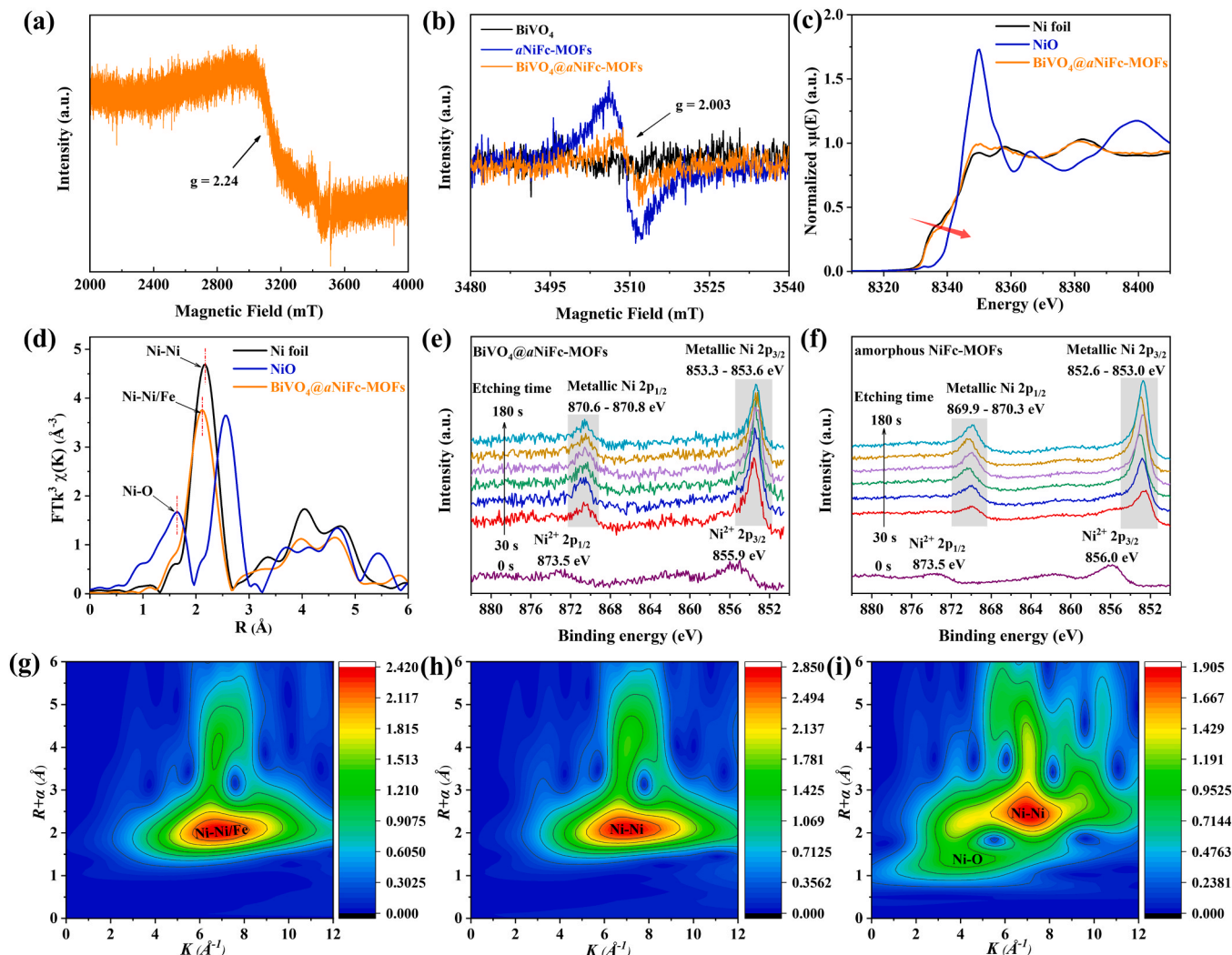


Fig. 3. (a)–(b) The EPR spectra of samples. (c) Ni K-edge XANES and (d) Fourier-transform EXAFS spectra of $\text{BiVO}_4@\text{aNiFc-MOFs}$ and reference samples. XPS argon-ion sputtering of (e) $\text{BiVO}_4@\text{aNiFc-MOFs}$ and (f) amorphous NiFc-MOF powders. The WT contour plots of (g) $\text{BiVO}_4@\text{aNiFc-MOFs}$, (h) Ni foil and (i) NiO.

edge X-ray absorption near-edge structure (XANES), the extended X-ray absorption fine structure (EXAFS) and XPS argon-ion sputtering measurements. The EPR spectra of $\text{BiVO}_4@\text{aNiFc-MOFs}$ in Fig. 3a, b shows a strong signal at $g = 2.24$ and 2.003 , which respectively correspond to Ni cationic vacancies (V_{Ni}) and O anion vacancies (V_{O}) [53]. Notably, compared with the extremely strong V_{O} signal of aNiFc-MOFs (Fig. 3b), weak V_{O} signal of pristine BiVO_4 could be almost negligible, suggesting that most of V_{O} was generated in aNiFc-MOFs . The rich existence of cationic and anion vacancy defects in the aNiFc-MOFs could facilitate forming plenty of coordinatively unsaturated Ni sites, thereby greatly enhancing the surface water oxidation kinetics of the photocatalyst. Moreover, the analysis of EXAFS curve fitting reveals that the average coordination number (CN) of Ni-O in $\text{BiVO}_4@\text{aNiFc-MOFs}$ is 1.1 ± 0.1 and the average CN of Ni-Ni is 10.7 ± 0.2 (Fig. S5 and Table S3). Typically, the perfect cNiFc-MOFs exhibited a CN around 6 of Ni-O [32, 37,54], further confirming the formation of abundant coordinatively unsaturated Ni sites in $\text{BiVO}_4@\text{aNiFc-MOFs}$. Surprisingly, the Ni K-edge XANES spectra of $\text{BiVO}_4@\text{aNiFc-MOFs}$ display the absorption edge position similar to Ni foil, suggesting the valence state of the Ni species in bulk is close to 0 (Fig. 3c). Meanwhile, the relevant Ni EXAFS spectra of both Ni foil and $\text{BiVO}_4@\text{aNiFc-MOFs}$ show a prominent peak around 2.1 \AA (Fig. 3d), consistent with the lengths of the second coordination Ni-Ni/Fe shell, which is confirmed by the wavelet transform (WT) results (Fig. 3g–i). These XAS conclusions demonstrate that the Ni species

in $\text{BiVO}_4@\text{aNiFc-MOFs}$ retained the metal-like state, which was different from the surface chemical state results obtained from the high-resolution XPS spectra of Ni 2p.

Given that the limited depth of characterization (1–10 nm) achievable by XPS on the surface of the sample, the XPS argon-ion sputtering test was conducted to further investigate the elemental chemical state both on the surface and in the bulk of $\text{BiVO}_4@\text{aNiFc-MOFs}$ (Fig. 3e, f). Consistent with the XPS spectra of Ni 2p, the element Ni on the surface of both $\text{BiVO}_4@\text{aNiFc-MOFs}$ photoanode and amorphous NiFc-MOF powders were attributed to the divalent Ni before argon-ion etching. As the etching time increases, the XPS characteristic peaks of Ni^{2+} diminished, and concomitantly, the characteristic peaks corresponding to metallic Ni became the dominant. This result confirmed that the Ni species in the bulk of aNiFc-MOFs loaded on the $\text{BiVO}_4@\text{aNiFc-MOFs}$ photoanode were metallic Ni. To eliminate potential systematic errors during the test, XPS sputtering measurements are conducted on the $\text{BiVO}_4@\text{cNiFc-MOFs}$ photoanode (Fig. S6a). The Ni 2p spectra was not changed within the etching process, suggesting that argon-ion etching had little impact on the oxidation state of Ni. Notably, the overall binding energies of metallic Ni 2p in $\text{BiVO}_4@\text{aNiFc-MOFs}$ were higher than those of aNiFc-MOFs . This observation suggested the presence of a distinctive chemical interaction between the metallic Ni in the bulk of aNiFc-MOFs and the supporting BiVO_4 semiconductor. Considering that the internal structure of $\text{BiVO}_4@\text{cNiFc-MOFs}$ was very similar to the typical supported

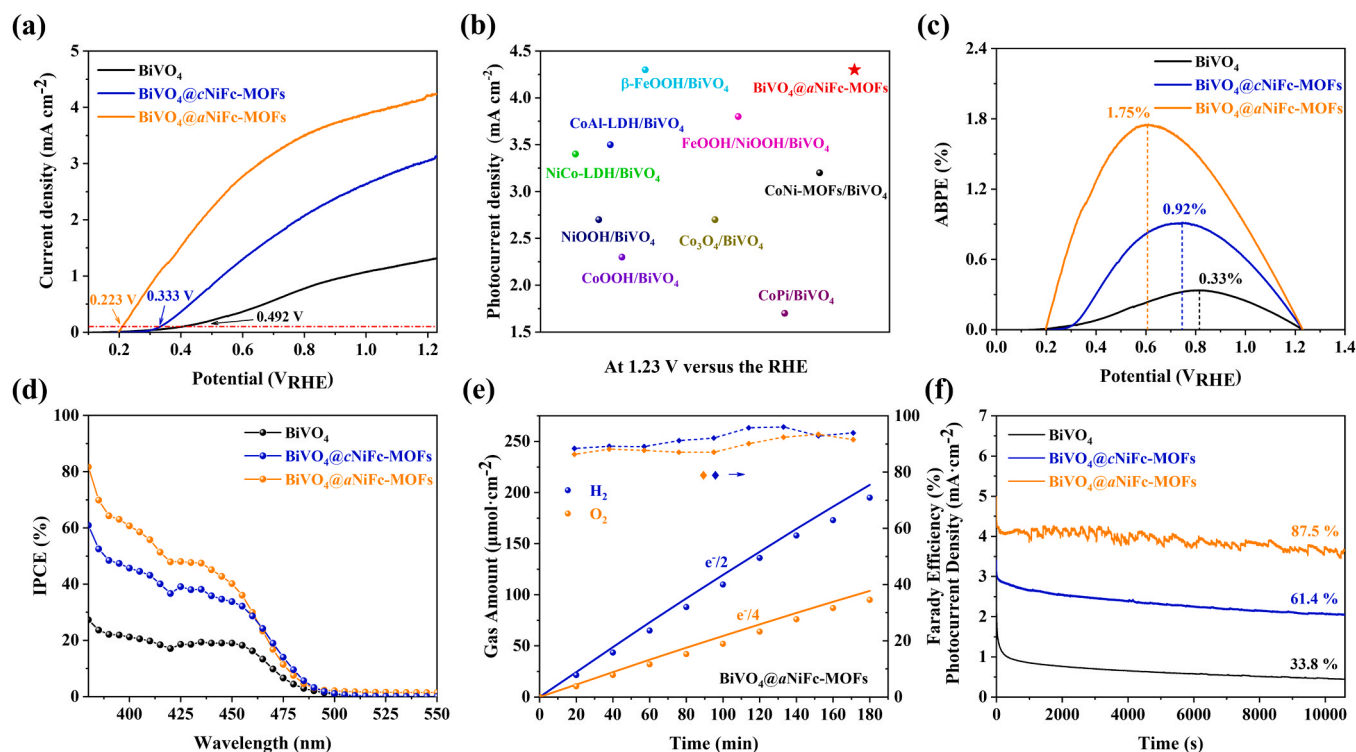


Fig. 4. (a) LSV. (b) Comparison of our photoanode with other common co-catalyst/BiVO₄ photoanodes. (c) ABPE and (d) IPCE of BiVO₄, BiVO₄@cNiFc-MOFs and BiVO₄@aNiFc-MOFs photoanodes. (e) H₂ and O₂ production at 1.23 V vs. RHE within 180 min and Faraday efficiencies for OER, HER. (f) Stability test at 1.23 V vs. RHE.

metal photocatalyst reported recently [55], such interaction might be the SMSI which could efficiently promote the interface charge. In addition, the XPS sputtering analysis of Fe 2p for the BiVO₄@aNiFc-MOFs photoanode and aNiFc-MOFs (Fig. S6b, c) reveals that the valence state of Fe element (notably the Fe-Fe²⁺) both in bulk and surface are almost the same.

Based on the above structure characterizations of samples, it could be concluded that the aNiFc-MOFs on BiVO₄@aNiFc-MOFs photoanode were actually short-range ordered with the complicated local atomic environment. Specifically, the surface structure of the BiVO₄@aNiFc-MOFs photoanode comprised a layer of NiFc-MOFs with abundant coordinatively unsaturated Ni sites, where the number of coordinated oxygen atoms (arising from the pair of carboxylate groups on each Fc unit) for Ni was less than six [32]. Nevertheless, its internal atomic structure underwent collapse during this distinctive growth process of MOF crystals. Local distortions in the aNiFc-MOFs resulted in bond breakages within the framework, consequently causing the Ni species in BiVO₄@aNiFc-MOFs to adopt a metal-like state. Therefore, due to the unique surface and internal structure, BiVO₄@aNiFc-MOFs photoanode had the potential to deliver a satisfactory PEC water splitting performance.

3.2. Photoelectrochemical water splitting performance

The PEC water splitting performance of all samples were studied under the simulated sun irradiation (100 mW cm⁻²) in 0.5 M KBI electrolyte. As expected, BiVO₄@aNiFc-MOFs (4.34 mA cm⁻²) achieves the highest photocurrent densities at 1.23 V_{RHE} among these samples [BiVO₄@cNiFc-MOFs (3.13 mA cm⁻²); BiVO₄ (1.31 mA cm⁻²)], and even superior to other common co-catalyst/BiVO₄ photoanodes reported in previous literatures (Fig. 4a, b) [48,56–64]. Meanwhile, the onset potential of BiVO₄@aNiFc-MOFs (0.223 V_{RHE}) can be obtained according to LSV curves (potential at the current density of 0.1 mA cm⁻²) [65], which displays the cathodic shifts of 110 mV and

269 mV compared with BiVO₄@cNiFc-MOFs and BiVO₄ (Fig. 4a), respectively. The ABPE representing solar energy conversion efficiency was determined by subtracting the contribution of bias voltage. This metric could be calculated based on the data extracted from LSV curves. BiVO₄@aNiFc-MOFs photoanode exhibits a maximum ABPE of 1.75% at a relatively low bias of 0.61 V_{RHE} (Fig. 4c). This value is approximately 1.9 times higher than the ABPE of BiVO₄@cNiFc-MOFs, recorded at 0.92% with a bias of 0.75 V_{RHE}, and 5.3 times higher than the ABPE of the BiVO₄, which is 0.33% at 0.81 V_{RHE}. It is noteworthy that the bias applied to achieve the peak ABPE aligns with the corresponding shifts in onset potentials. Moreover, the BiVO₄@aNiFc-MOFs photoanode exhibits the highest IPCE among all the samples, spanning the entire wavelength range from 400 to 550 nm (Fig. 4d). In the quantitative gas test, the yields of hydrogen and oxygen are respectively determined to be 195.5 and 97.7 μmol after a 180-minute duration, with corresponding Faradaic efficiencies of 92.1% for hydrogen and 89.3% for oxygen (Fig. 4e). Such significant improvements of PEC performance highlighted the superiority of aNiFc-MOFs as an OER co-catalyst which could effectively boost the water oxidation activity.

To evaluate the potential practical applications, stability tests were conducted on the samples at 1.23 V vs. RHE for a duration of 3 hours (Fig. 4f). The BiVO₄@aNiFc-MOFs photoanode can maintain 87.5% of the initial photocurrent density within 3 hours. In stark contrast, both BiVO₄ and BiVO₄@cNiFc-MOFs exhibit considerable photocurrent loss. Compared to the BiVO₄@cNiFc-MOFs with nanosheet embedded morphology (Fig. S2c), the higher stability of BiVO₄@aNiFc-MOFs could be attributed to the conformal coating by the core-shell structure (Fig. 1a and Fig. S2b) which prevented V⁵⁺ in BiVO₄ lattice from dissolving into electrolyte [66]. Moreover, the existence of SMSI could facilitate the formation of V-O-Ni interfacial bonds, also effectively restraining the dissolution of V⁵⁺ ions from the BiVO₄ lattice [67], thereby enhancing the photoelectrochemical stability. On the other hand, reconstruction of MOFs under alkaline conditions may influence the stability. Herein, the CV and in-situ Raman characterizations demonstrated that both

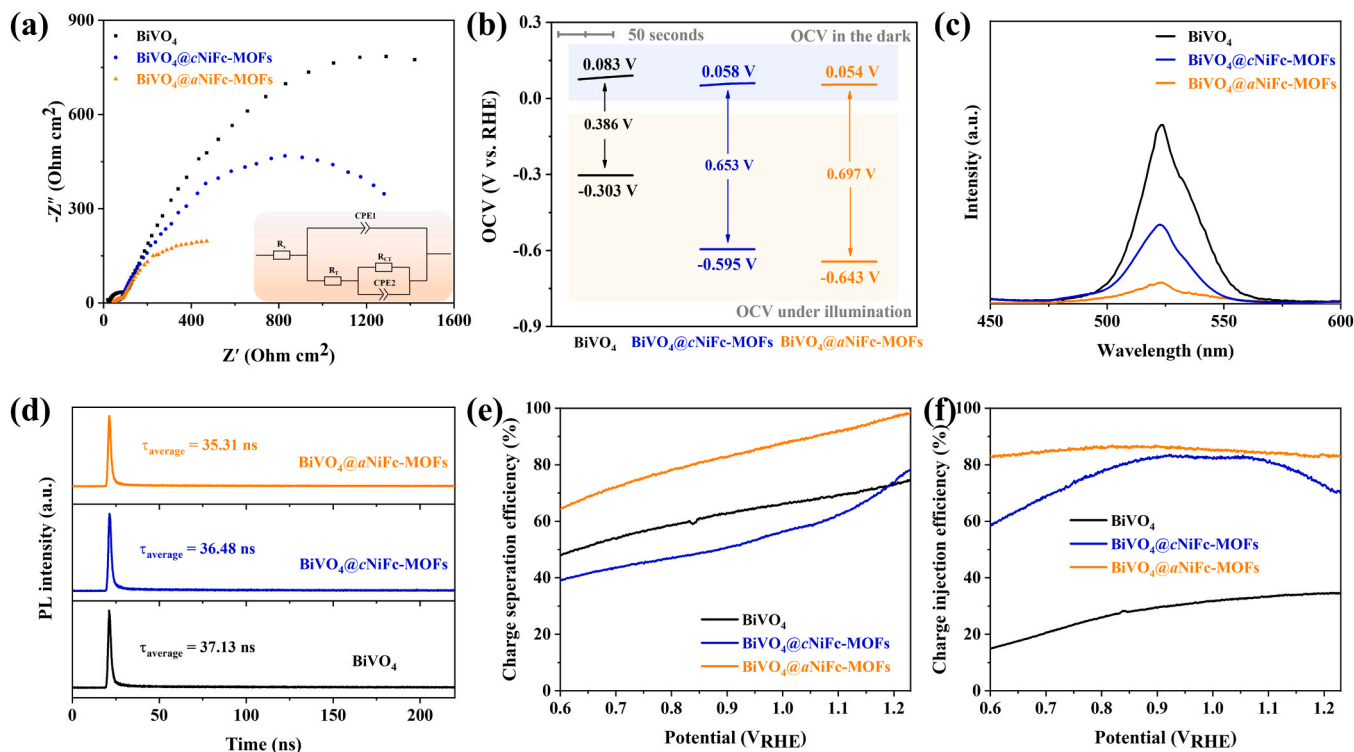


Fig. 5. (a) EIS Nyquist plots at 0.2 V_{RHE} under AM 1.5 G illumination (inset is the two-RC-unit equivalent circuit). (b) OCP decay profile. (c) PL and (d) TRPL spectra of BiVO₄, BiVO₄@cNiFc-MOFs and BiVO₄@aNiFc-MOFs photoanodes. (e) η_{sep} and (f) η_{inj} of three photoanodes.

BiVO₄@aNiFc-MOFs and BiVO₄@cNiFc-MOFs photoanodes did not undergo reconstruction during PEC water splitting (Text S2, Fig. S7–8).

3.3. Possible mechanism analysis

To explore the underlying catalytic mechanism of the overall improved PEC performance of BiVO₄@aNiFc-MOFs, carrier kinetic and surface water oxidation kinetic were analyzed by systematic characterizations. In comparison with the BiVO₄ photoanode, the UV–vis absorption spectra of the BiVO₄@aNiFc-MOFs photoanode exhibit an improved absorbance behavior with similar cut-off edges at 504 nm (Fig. S9a), corresponding to a band gap of approximately 2.49 eV (Fig. S9b). However, its light absorption capacity is slightly weaker than that of the BiVO₄@cNiFc-MOFs photoanode. Despite this, considering its superior water oxidation performance among all the samples, this unusual phenomenon precisely highlighted the unique catalytic capabilities of the BiVO₄@aNiFc-MOFs photoanode, in addition to its optical properties. Electrochemical characterizations such as M-S spectra, PEIS and open circuit potential (OCP) decay were then measured to evaluate the electronic behavior of photoanodes. The carrier density (N_d) of BiVO₄@aNiFc-MOFs is calculated to be $3.10 \times 10^{20} \text{ cm}^{-3}$ from the M-S spectra (Fig. S10 and Table S4), approximately 5.1 and 2.3 times higher than that of BiVO₄ ($6.09 \times 10^{19} \text{ cm}^{-3}$) and BiVO₄@cNiFc-MOFs ($1.38 \times 10^{20} \text{ cm}^{-3}$), respectively, suggesting the robust electronic conductivity of BiVO₄@aNiFc-MOFs. This experimental result could be attributed to the increased donor density resulting from the introduction of cationic and anion vacancy defects during the amorphization of NiFc-MOFs, along with the strong metal conductivity of metallic Ni in the bulk of the BiVO₄@aNiFc-MOFs photoanode. A conventional two-RC-unit equivalent circuit (inserted in Fig. 5a) is employed to fit the Nyquist plots of PEIS (Fig. 5a). In this context, R_s typically represented a series resistance encompassing the electrolyte, external contact, and conductive substrate, while R_t denoted the bulk charge transfer resistance, and R_{CT} denoted the photoanode-electrolyte junction charge transfer resistance [68]. As outlined in Table S5, the R_t values for the

samples follow the order of BiVO₄@aNiFc-MOFs (112.2 Ω) < BiVO₄@cNiFc-MOFs (154.3 Ω) < BiVO₄ (191.8 Ω). This sequence highlighted the central role of metallic Ni in the bulk of BiVO₄@aNiFc-MOFs in accelerating carrier migration. The metal-like state of Ni in aNiFc-MOFs established an intimate interface with the supporting semiconductor BiVO₄, resembling a heterojunction and denoting as the strong metal-support interaction. Such SMSI could significantly promote interfacial charge separation, thereby enhancing the PEC water splitting activity. Moreover, the OCP decay profile provides additional insights into interfacial charge separation (Fig. 5b). In comparison with BiVO₄ and BiVO₄@cNiFc-MOFs, the BiVO₄@aNiFc-MOFs photoanode, featuring a SMSI between metallic Ni and BiVO₄, exhibits a significantly accelerated OCP decay, indicative of a larger photovoltage generation (0.697 V). This observation demonstrated that the distinctive SMSI can provide an additional driving force to promote charge separation at the interface.

Generally, PL was associated with radiative recombination, while charge separation by a junction or non-radiative recombination was responsible for quenching PL intensity and short lifetime [24]. The notably reduced PL intensity of BiVO₄@aNiFc-MOFs suggests that the introduction of aNiFc-MOFs on BiVO₄ successfully enhances the interfacial hole extraction capability, thereby suppressing carrier recombination (Fig. 5c). As expected, the BiVO₄@aNiFc-MOFs photoanode with the lowest PL intensity possesses the shortest carrier lifetime (Fig. 5d and Table S6), further confirming the enhanced charge separation by SMSI through carrier dynamics on time scales. Both charge separation (η_{sep}) and charge injection efficiencies (η_{inj}) are calculated by using Na₂SO₃ as a hole scavenger according to the Eqs. 7 and 8 (Fig. 5e, f and Fig. S11a). J_{abs} in Eq. 7 for BiVO₄, BiVO₄@cNiFc-MOFs and BiVO₄@aNiFc-MOFs photoanodes are determined to be approximately 5.10, 5.68 and 5.20 mA cm⁻², respectively (Fig. S11b-d). Due to the fast kinetics for sulfite oxidation, the photogenerated holes reaching the interface between the photoanode and electrolyte would be promptly consumed. Consequently, a much high η_{sep} up to 98% (Fig. 5e) is achieved by BiVO₄@aNiFc-MOFs photoanode at 1.23 V_{RHE}, indicating that almost all

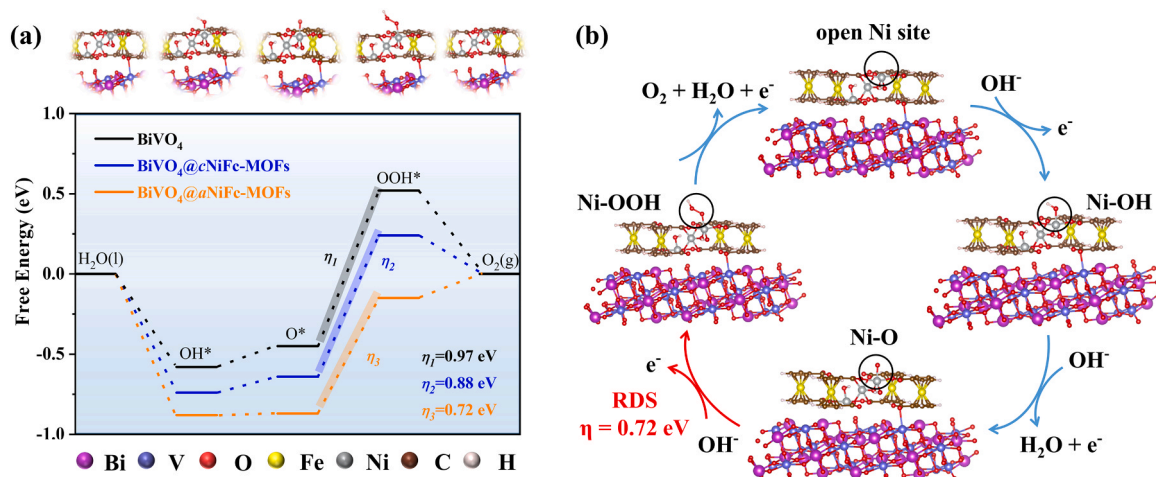


Fig. 6. (a) Gibbs free energy profile for OER on BiVO₄, BiVO₄@cNiFc-MOFs and BiVO₄@aNiFc-MOFs photoanodes. (b) Different adsorption intermediates for coordinatively unsaturated Ni sites in BiVO₄@aNiFc-MOFs photoanode.

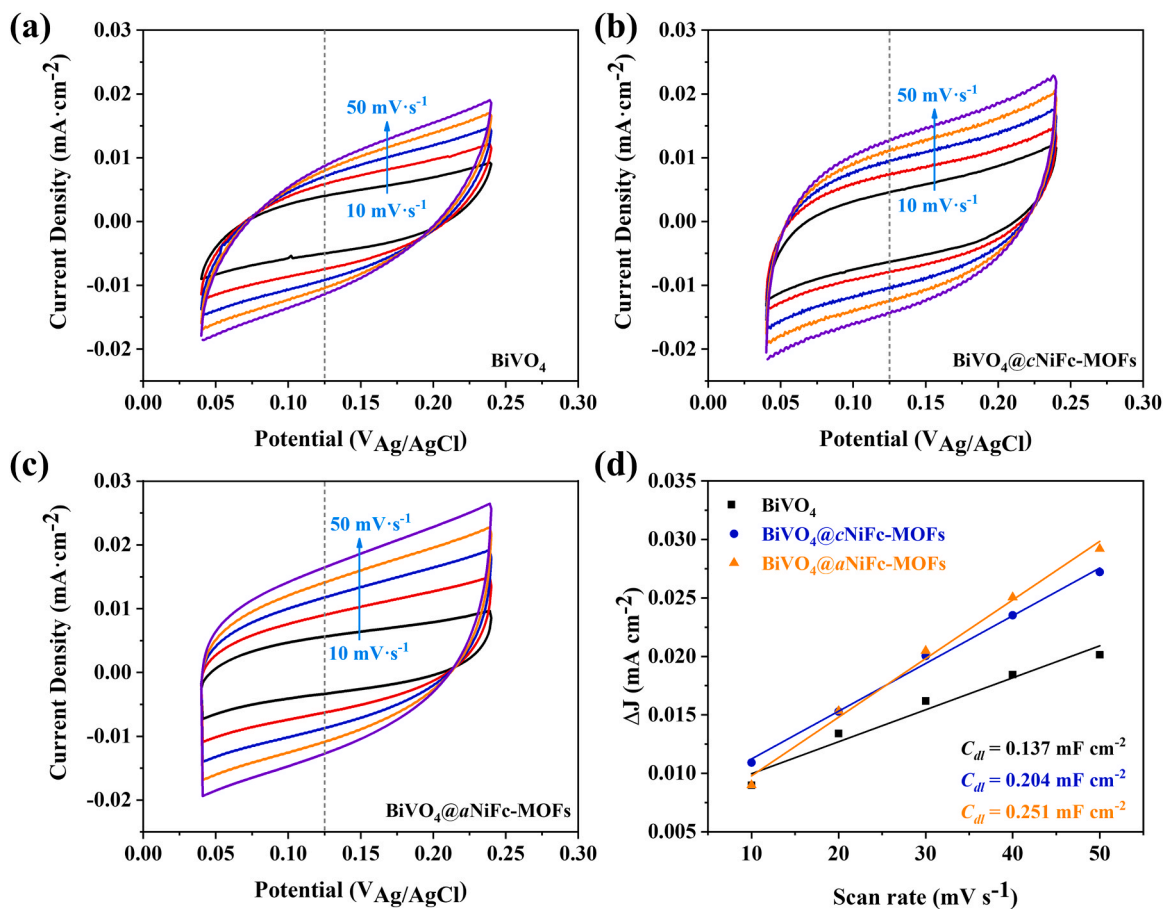


Fig. 7. (a)-(c) CV curves with different scan rates for BiVO₄, BiVO₄@cNiFc-MOFs and BiVO₄@aNiFc-MOFs photoanodes. (d) Linear fitting of the CV curves.

the photogenerated carriers in bulk can be separated efficiently and transfer to electrode surface without recombination. In addition, the enhancement of the η_{inj} for BiVO₄@aNiFc-MOFs also demonstrates the accelerated carriers transfer dynamics (Fig. 5f).

To gain direct insights into the role of aNiFc-MOFs with abundant coordinatively unsaturated Ni sites in mediating the OER catalytic mechanism, DFT calculations were employed by constructing optimized models of aNiFc-MOFs and perfect cNiFc-MOFs on BiVO₄. The active site for the pristine BiVO₄ photoanode was the V atom [69]. In contrast, the

active sites Ni were considered as adsorption sites for OER intermediates for the models of BiVO₄@cNiFc-MOFs and BiVO₄@aNiFc-MOFs photoanodes [32,37]. Following the four-electron transfer mechanism, the Gibbs free energy (ΔG) was calculated for each step of the OER, encompassing the adsorption of different oxygen intermediates (OH*, O*, OOH*, and O₂), with an additional potential ($U = 1.23$) (Fig. 6a). In comparison with BiVO₄@cNiFc-MOFs, the BiVO₄@aNiFc-MOFs exhibits the lower energy barrier of the first adsorption step (*→OH*), which agrees well with the higher hydrophilicity with a contact angle of 52.14°

(Fig. S12). All the samples share the same rate-determining step of the conversion from O^* to OOH^* . Remarkably, the $BiVO_4@aNiFc$ -MOFs photoanode exhibits a ΔG of 0.72 eV for the formation of OOH^* , much lower than that of $BiVO_4@cNiFc$ -MOFs (0.88 eV) and $BiVO_4$ (0.97 eV) (Fig. 6a, b). In conclusion, compared with other photoanodes, the OER over the coordinatively unsaturated Ni sites of $BiVO_4@aNiFc$ -MOF exhibited a more favorable pathway for adsorbing O adsorbates, especially for the rate-determining step of adsorbing *OOH . Thus, such $aNiFc$ -MOFs with abundant coordinatively unsaturated Ni sites on $BiVO_4$ could thermodynamically facilitate surface water oxidation.

For further confirmation of the enhanced OER adsorption and activation behaviors, the electrochemical active surface area (ECSA) of the photoanodes was estimated through the electrochemical double layer capacitances (C_{dl}) obtained from CV curves (Fig. 7). As anticipated, $BiVO_4@aNiFc$ -MOFs achieves a C_{dl} of 0.251 mF cm^{-2} , significantly higher than that of $BiVO_4@cNiFc$ -MOFs (0.204 mF cm^{-2}) and $BiVO_4$ (0.137 mF cm^{-2}) (Fig. 7d), indicating a substantial increase in active sites due to the exposure of coordinatively unsaturated Ni sites on the surface of $BiVO_4@aNiFc$ -MOFs. In addition, compared with $BiVO_4@cNiFc$ -MOFs, the η_{inj} of $BiVO_4@aNiFc$ -MOFs (Fig. 5f) is higher over the potential range from 0.6 to $1.23 V_{RHE}$. This result suggested that more holes from the $BiVO_4@aNiFc$ -MOFs photoanode participates in water oxidation, even under relatively low overpotential. Moreover, the dark LSV curves (Fig. S13) reveal that $BiVO_4@aNiFc$ -MOFs exhibits an earlier onset potential and faster increase of current density compared to other photoanodes, highlighting the excellent catalytic activity of the co-catalyst $aNiFc$ -MOFs with abundant coordinatively unsaturated Ni sites.

4. Conclusion

In this study, the crystallinity of NiFc-MOFs is precisely controlled via changing the concentration of metal ions and organic linkers. The $aNiFc$ -MOFs were successfully integrated onto the $BiVO_4$ photoanode for PEC water splitting, which displays an outstanding photocurrent density of 4.34 mA cm^{-2} at $1.23 V_{RHE}$ with a relatively low onset potential of $0.223 V_{RHE}$. The subsequent structural and carrier kinetic experiments confirmed the distinctive electronic and atomic structure of the $BiVO_4@aNiFc$ -MOFs photoanode, where the surface is the $aNiFc$ -MOFs layer with abundant coordinatively unsaturated Ni sites and the internal Ni species adopt a metal-like state. Being attributed to the SMSI formed between the metallic Ni and $BiVO_4$, interfacial charge transfer and separation are significantly accelerated, resulting in great improvement of OER activity. Meanwhile, abundance of coordinatively unsaturated Ni sites on $BiVO_4@aNiFc$ -MOFs can provide additional highly active adsorption sites for OER intermediates, creating a more favorable pathway for OER based on thermodynamics. The present work not only provide an efficient photoanode for OER, but also boost the application of α -MOFs in PEC water splitting technology.

CCRediT authorship contribution statement

Weihao Bai: Conceptualization, Investigation, Methodology, Writing – original draft. **Hao Li:** Conceptualization, Investigation, Methodology, Writing – original draft. **Gang Peng:** Conceptualization, Data curation, Visualization. **Jinnan Wang:** Conceptualization, Project administration, Supervision, Writing – review & editing. **Aimin Li:** Writing – review & editing. **Philippe François-Xavier Corvini:** Visualization.

Declaration of Competing Interest

We have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

No data was used for the research described in the article.

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Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.apcatb.2024.124023.

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